*Inorganica Chimica Acta*, *156* (1989) 195–200

# Mercury(II) Halide Complexes of Tertiary Phosphines
# Part XII*. Crystal Structure of $[(NCCH_2CH_2)_3P]_2HgCl_2$ and Comparisons with other $(R_3P)_2HgX_2$ Complexes

NORMAN A. BELL**, LORRAINE A. MARCH and IAN W. NOWELL†

*Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield S1 1WB, U.K.*

(Received June 8, 1988)

## Abstract

The X-ray crystal structure of $[(NCCH_2CH_2)_3P]_2$-$HgCl_2$ shows that the complex is monoclinic, space group $P2_1/c$, with $a = 25.728(8)$, $b = 8.627(2)$, $c = 24.482(8)$ Å, $\beta = 115.14(1)°$. The structure was solved by the heavy atom method and refined to a final $R$ value of 0.062 for 2522 observed diffractometer data. The structure consists of two independent highly distorted tetrahedral monomer units with the cyanoethyl groups disordered. The coordination polyhedron around mercury is increased beyond four by one weak $\pi$-interaction in one unit and two in the other unit involving the cyano groups and mercury. Comparison of Hg–P distances and P–Hg–P angles with those found for other 2:1 tertiary phosphine–mercury(II) halide complexes shows that despite the low $pK_a$ value for 2-cyanoethylphosphine it is a strong $\sigma$-donor to mercury(II) halides, a result further confirmed by $^{31}P$ NMR data.

## Introduction

Our earlier work has shown that while a range of structural types have been established for 1:1 tertiary phosphine mercury(II) halides, $R_3P{\cdot}HgX_2$, ranging from dimers, through tetramers, to five and six coordinate polymers [1–9], the 2:1 complexes $(R_3P)_2HgX_2$ have a monomeric pseudotetrahedral constitution [9–12]. Structural variations appear to be markedly influenced by the electronic nature of the substituents attached to phosphorus as well as by the steric requirement of the phosphine. In order to establish the relative importance of these two effects we have examined the coordination characteristics of tris(2-cyanoethyl)phosphine which forms readily isolable crystalline 1:1 and 2:1 complexes with mercury(II) halides. Though this phosphine is sterically similar to the strong $\sigma$-donor triethylphosphine in the region of coordination, it has a much lower basicity ($pK_a$, 1.37) than triethylphosphine ($pK_a$, 8.69) [13] and other simple tertiary phosphines. The geometry and molecular parameters of the 1:1 complex $[(NCCH_2CH_2)_3P{\cdot}HgCl_2]_n$ unequivocally establish that this phosphine is also a strong $\sigma$-donor to mercury(II) halides, comparable with triethylphosphine [9]. Thus, although the electron-withdrawing property of the cyanoethyl group lowers the $pK_a$ compared to triethylphosphine, it does not significantly reduce the coordinative ability of the substituted phosphine in its interaction with mercury(II) halides.

The molecular parameters for the 2:1 complex $((NCCH_2CH_2)_3P)_2HgBr_2{\cdot}Me_2CO$ tended to confirm the same conclusion and also the far infrared spectra of all three complexes $((NCCH_2CH_2)_3P)_2HgX_2$, (X = Cl, Br, I) were similar to those of the $Et_3P$ and $Bu_3P$ rather than the $Ph_3P$ analogues [9]. Unfortunately the X-ray structure showed that this complex contained one mole of acetone within the coordination sphere of the metal and this may affect the parameters (especially the PHgP angle) we have used to compare donor strength of tertiary phosphines to mercury(II) halides. In order to provide data for meaningful comparison with other analogous tertiary phosphine–mercury(II) halide systems we have now determined the crystal structure of the solvent-free complex $((NCCH_2CH_2)_3P)_2$-$HgCl_2$ and obtained the $^{31}P$ NMR spectra of it and the bromide and iodide analogues.

## Experimental

### *Crystallographic Studies*

The complex was prepared as described earlier [9] and recrystallised from acetone as colourless needles. A crystal of approximate dimensions 0.08 × 0.48 × 0.04 mm was mounted with its $b$ axis coincident with the $\omega$-axis of a Stöe Stadi 2 two circle

---

*For part XI: see ref. 7.

**Author to whom correspondence should be addressed.

†Present address: School of Chemistry, Robert Gordon's Institute of Technology, St. Andrew Street, Aberdeen AB1 1HG, U.K.

0020-1693/89/$3.50

diffractometer. Data were collected using the background-ω scan-background technique and with graphite monochromated Mo Kα radiation. 4241 unique reflections were measured of which 2522 had $I/\sigma(I) \geqslant 3.0$ and were used for subsequent analysis. Data were corrected for Lorentz and polarisation effects but absorption corrections were not applied.

### *Crystal data*

$C_{18}H_{24}Cl_2N_6HgP_2$, $M = 657.9$, monoclinic, $a = 25.728(8)$, $b = 8.627(2)$, $c = 24.482(8)$ Å, $\beta = 115.14(1)^\circ$, $U = 4919.5$ Å$^3$, $F(000) = 2544$, space group $P2_1/c$, $Z = 8$, $D_m$ (by flotation) = 1.80, $D_c$ = 1.78 g cm$^3$, Mo Kα radiation, $\lambda = 0.71069$ Å, $\mu$(Mo Kα) = 63.6 cm$^{-1}$.

The structure was solved using the heavy atom method and refined by full-matrix least squares. There was some degree of disorder in the cyanoethyl groups and it proved difficult to resolve this satisfactorily and also made it impossible to include any hydrogen atoms in the structure analysis. Hence anisotropic temperature factors were only applied to mercury, phosphorus and chlorine atoms and all the remaining atoms were treated isotropically. Locating and refining the cyanoethyl groups proved so difficult that despite the rather unsatisfactory geometry, the positions of the carbon and nitrogen atoms were fixed in the final stages of the analysis. Complex neutral-atom scattering factors [14] were employed and in the final cycles of refinement the weighting scheme $W = 1.000/[\sigma^2(F_o) + 0.001296\,(F_o)^2]$ was adopted. Final refinement converged at $R = 0.062$, $R' = 0.064$. Final positional parameters are listed in Table 1, bond distances and angles in Table 2. All calculations were performed using an IBM 4341 computer using the SHELX computing package [15].

### *NMR Studies*

Phosphorus-31 NMR spectra were recorded as solutions in deuterioacetone at 32.44 MHz using a Bruker WP80SY 80 MHz spectrometer. Chemical shifts are reported on the δ scale with respect to

TABLE 1. Final Fractional Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Mercury, Chlorine and Phosphorus Atoms[a]

| | Molecule I | | | Molecule II | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| Hg | 1638(1) | 1948(2) | 4198(1) | 6578(0) | 2437(2) | 2564(1) |
| Cl(1) | 1606(5) | −721(11) | 4683(4) | 7244(4) | 1005(11) | 2132(4) |
| Cl(2) | 2215(4) | 3363(14) | 5228(4) | 6806(4) | 5281(11) | 2385(5) |
| P(1) | 2256(4) | 1341(12) | 3692(4) | 7179(3) | 1856(10) | 3608(3) |
| P(2) | 724(4) | 3050(14) | 4100(4) | 5706(3) | 2188(11) | 1622(3) |
| C(11) | 2526 | −683 | 3827 | 7482 | −116 | 3717 |
| C(12) | 2030 | −1759 | 3526 | 7068 | −1378 | 3361 |
| C(13) | 2308 | −2934 | 3851 | 6712 | 8508 | 3556 |
| N(13) | 2454 | −4258 | 4183 | 6372 | 7864 | 3828 |
| C(21) | 1906 | 1497 | 2849 | 7858 | 2999 | 3934 |
| C(22) | 1741 | 3003 | 2582 | 8131 | 3036 | 3517 |
| C(23) | 1445 | 3828 | 2812 | 8630 | 3979 | 3758 |
| N(23) | 1163 | 4674 | 3022 | 9131 | 4322 | 4125 |
| C(31) | 2886 | 2434 | 3896 | 6890 | −8001 | 4160 |
| C(32) | 3223 | 2437 | 4631 | 6768 | −6546 | 4263 |
| C(33) | 3711 | 3585 | 4795 | 6329 | −5792 | 3897 |
| N(33) | 4117 | 4336 | 5017 | 5869 | −5518 | 3414 |
| C(41) | 118 | 3060 | 3377 | 5427 | 265 | 1383 |
| C(42) | −201 | 1525 | 3072 | 5881 | −929 | 1514 |
| C(43) | 160 | 877 | 3126 | 5697 | −2320 | 1148 |
| N(43) | 606 | 4 | 2942 | 5556 | −3392 | 903 |
| C(51) | 852 | 5327 | 4155 | 5052 | 3109 | 1611 |
| C(52) | 627 | 5593 | 4510 | 5164 | 4579 | 1841 |
| C(53) | 307 | 6464 | 4035 | 4769 | 5510 | 1942 |
| N(53) | −203 | 6997 | 3204 | 4340 | 5382 | 2089 |
| C(61) | 447 | 2158 | 4577 | 5941 | 2989 | 1063 |
| C(62) | 908 | 2500 | 5166 | 5449 | 3004 | 406 |
| C(63) | 819 | 1509 | 5353 | 5740 | 3652 | 39 |
| N(63) | 638 | 700 | 5844 | 5916 | 4264 | −277 |

[a] Positions of carbon and nitrogen atoms were not refined in the final stages of the analysis.

TABLE 2. Bond Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

| | Molecule I | Molecule II | | Molecule I | Molecule II |
|---|---|---|---|---|---|
| Distances (Å) | | | | | |
| Hg–Cl(1) | 2.608(10) | 2.669(11) | Hg–Cl(2) | 2.622(1) | 2.603(10) |
| Hg–P(1) | 2.450(12) | 2.411(7) | Hg–P(2) | 2.452(11) | 2.450(6) |
| P(1)–C(11) | 1.86 | 1.84 | P(2)–C(41) | 1.80 | 1.80 |
| P(1)–C(21) | 1.87 | 1.87 | P(2)–C(51) | 1.99 | 1.85 |
| P(1)–C(31) | 1.76 | 1.80 | P(2)–C(61) | 1.78 | 1.85 |
| C(11)–C(12) | 1.50 | 1.51 | C(41)–C(42) | 1.57 | 1.49 |
| C(12)–C(13) | 1.30 | 1.20 | C(42)–C(43) | 1.04 | 1.45 |
| C(13)–N(13) | 1.36 | 1.42 | C(43)–N(43) | 1.59 | 1.08 |
| C(21)–C(22) | 1.44 | 1.46 | C(51)–C(52) | 1.25 | 1.37 |
| C(22)–C(23) | 1.33 | 1.42 | C(52)–C(53) | 1.34 | 1.40 |
| C(23)–N(23) | 1.28 | 1.26 | C(53)–N(53) | 1.95 | 1.30 |
| C(31)–C(32) | 1.63 | 1.34 | C(61)–C(62) | 1.46 | 1.57 |
| C(32)–C(33) | 1.51 | 1.28 | C(62)–C(63) | 1.04 | 1.50 |
| C(33)–N(33) | 1.15 | 1.29 | C(63)–N(63) | 1.62 | 1.18 |
| Angles (°) | | | | | |
| Cl(1)–Hg–Cl(2) | 95.0(3) | 98.1(3) | P(1)–Hg–P(2) | 146.6(3) | 153.9(3) |
| Cl(1)–Hg–P(1) | 101.2(4) | 95.4(3) | Cl(2)–Hg–P(2) | 92.3(3) | 96.1(3) |
| Cl(1)–Hg–P(2) | 100.0(4) | 94.1(3) | Cl(2)–Hg–P(1) | 111.2(3) | 106.6(3) |
| Hg–P(1)–C(11) | 113(2) | 113(2) | Hg(1)–P(2)–C(41) | 120(1) | 118(1) |
| Hg–P(1)–C(21) | 116(2) | 114(1) | Hg(1)–P(2)–C(51) | 105(1) | 116(1) |
| Hg–P(1)–C(31) | 118(2) | 120(1) | Hg(1)–P(2)–C(61) | 114(2) | 102(1) |
| C(11)–P(1)–C(21) | 103 | 99 | C(41)–P(2)–C(51) | 96 | 99 |
| C(11)–P(1)–C(31) | 103 | 104 | C(41)–P(2)–C(61) | 103 | 108 |
| C(21)–P(1)–C(31) | 103 | 105 | C(51)–P(2)–C(61) | 119 | 114 |
| P(1)–C(11)–C(12) | 109 | 115 | P(2)–C(41)–C(42) | 122 | 114 |
| C(11)–C(12)–C(13) | 93 | 107 | C(41)–C(42)–C(43) | 98 | 115 |
| C(12)–C(13)–N(13) | 164 | 161 | C(42)–C(43)–N(43) | 158 | 176 |
| P(1)–C(21)–C(22) | 119 | 111 | P(2)–C(51)–C(52) | 119 | 111 |
| C(21)–C(22)–C(23) | 114 | 110 | C(51)–C(52)–C(53) | 78 | 124 |
| C(22)–C(23)–N(23) | 178 | 155 | C(52)–C(53)–N(53) | 159 | 140 |
| P(1)–C(31)–C(32) | 108 | 114 | P(2)–C(61)–C(62) | 100 | 113 |
| C(31)–C(32)–C(33) | 107 | 123 | C(61)–C(62)–C(63) | 92 | 103 |
| C(32)–C(33)–N(33) | 168 | 158 | C(62)–C(63)–N(63) | 150 | 173 |

85% $H_3PO_4$ and are accurate to ±0.1 ppm. Shifts to high field are positive in sign. Coupling constants are reported in Hz and are accurate to ±1.2 Hz.

## Results and Discussions

In contrast to the structure of the 1:1 complex $[(NCC_2H_4)_3P{\cdot}HgCl_2]_n$ which has a single chain polymeric structure consisting of almost linear $ClHgPR_3$ units bridged by further chlorine atoms [9], the X-ray analysis of the 2:1 complex, $[(NCC_2H_4)_3P]_2HgCl_2$ shows it to be monomeric like the other 2:1 tertiary phosphine–mercury(II) halide complexes examined [10–12]. There are two independent monomer units in the unit cell with the mercury atoms in both units in highly distorted tetrahedral environments with angles around mercury varying from 92.3(3)° to 146.6(3)° in molecule **I** (Fig. 1) and 94.1(3)° to 153.9(3)° in molecule **II** (Fig. 2). All the cyanoethyl groups are disordered to some degree resulting in high errors and widely varying C–C (1.04(15)–1.63(5) Å) and C–N (1.08(3)–1.95(8) Å) bond distances, the largest variation being found in the bond lengths for C(*A*2)–C(*A*3) and C(*A*3)–N(*A*3) (*A* = 1–6).

In molecule **II** one of the cyanoethyl groups is orientated to facilitate a weak π-interaction between the cyano group and mercury (Fig. 2). Two such interactions are evident in molecule **I** involving one cyano group on both phosphorus atoms (Fig. 1). Such a π-interaction has also been found in the 1:1 complex $[(NCC_2H_4)_3PHgCl_2]_n$ [9] which has similar Hg–––C and Hg–––N distances to those found in molecule **I** and are somewhat shorter than those in molecule **II** (Table 3) but all are longer than the sum of the van der Waals radii (Hg–C, 2.40; Hg–N 2.30 Å [16]) indicating the interaction is weak. Such an interaction is absent in the trigonal bipyramidal structure of $[(NCC_2H_4)_3P]_2HgBr_2{\cdot}Me_2CO$

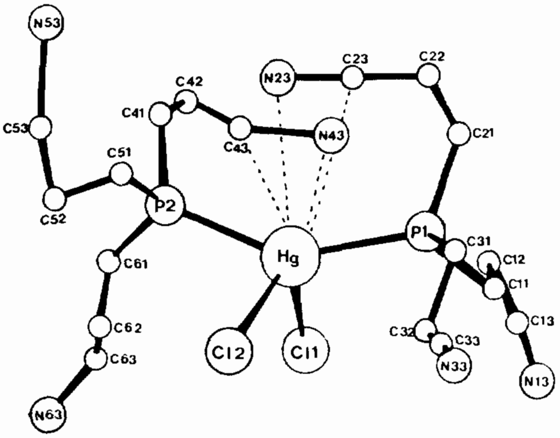

Fig. 1. Molecular structure of $((NCC_2H_4)_3P)_2HgCl_2$, molecule I.

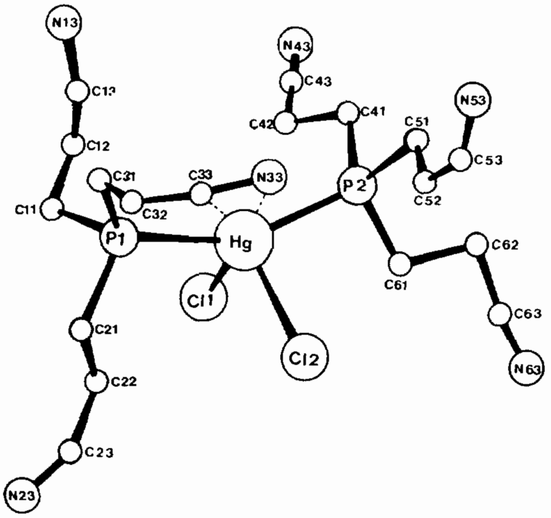

Fig. 2. Molecular structure of $((NCC_2H_4)_3P)_2HgCl_2$, molecule II.

TABLE 3. Comparison of C≡N π-Interactions in $((NCC_2H_4)_3P)_nHgCl_2$ ($n$ = 1 or 2)

| $n$ | Hg–C (Å) | Hg–N (Å) | Reference |
|---|---|---|---|
| 1 | 3.41(3), 3.65(3) | 3.58(3), 3.47(3) | 9 |
| 2 (Mol. I) | 3.60, 3.70 | 3.51, 3.52 | this work |
| (Mol. II) | 3.89 | 3.74 | |

due to the presence of the molecule of acetone within the coordination sphere of the metal. Thus the coordination arrangement around mercury could be construed as 6-coordinate in molecule **I** and 5-coordinate in molecule **II**, both highly distorted from regular shapes. The presence of two π-interactions in molecule **I** causes a reduction in the P–Hg–P angle compared to that found in molecule **II**.

Comparative data of selected molecular parameters in these two units together with those of other 2:1 tertiary phosphine–mercury(II) halide complexes are listed in Table 4. As with the other 2:1 complexes studies, the P–Hg–P angle is tending towards linearity, the ability of phosphorus to encourage mercury to adopt linear coordination being a reflection of the strength of the Hg–P interaction. As bromine is more strongly σ-donating to mercury than chlorine a similar trend to that found for the series $(Ph_3P)_2HgX_2$ (X = Cl, Br, I) where the stronger σ-donating bromide and iodide complexes have the smaller P–Hg–P angles is expected [10, 18]. In this case however, molecule **I** has a smaller P–Hg–P angle and molecule **II** a larger one than the bromide but in view of the effects of the molecule of acetone of crystallisation on the structure such comparisons are not valid.

From Table 4 it is clear that phosphines with the higher p$K_a$ values are the stronger σ-donors to mercury in having the shorter Hg–P distance and larger P–Hg–P angles. These parameters for $[(NCC_2H_4)_3P]_2HgCl_2$, particularly the P–Hg–P angle, are comparable with those for the strong σ-donor $Et_3P$ but differ markedly from those of the weaker donors $Ph_3P$ and (2-thienyl)$_3$P. Thus the structural data for the 2:1 complex $[(NCC_2H_4)_3P]_2HgCl_2$ reinforces the conclusions from the 1:1 complex that tris(2-cyanoethyl)phosphine like triethylphosphine is a strong σ-donor to mercury(II) halides and is markedly different in its donor characteristics to (2-thienyl)$_3$P and $Ph_3P$. Thus while the electron-withdrawing properties of the cyano groups lower the p$K_a$ compared to $Et_3P$ they do not appear to reduce the coordinating ability of the substituted phosphine to mercury(II) halides.

Using the criteria of relative Hg–P distances and P–Hg–P angles, the σ-donor strength to mercury(II) halides in the 2:1 complexes $(R_3P)_2HgX_2$ varies in the order:

$$Et_3P > (NCC_2H_4)_3P > EtMe_2P > Bu_3P > Ph_3P > (2\text{-}C_4H_3S)_3P$$

Although the data is much more limited, the mercury(II) bromide complexes show a similar trend, so that for $(R_3P)_2HgBr_2$ ($R_3P = (NCC_2H_4)_3P$, $EtMe_2P$, $Ph_3P$) the average Hg–P distances (2.440(3), 2.45(6), 2.537(16) Å) and P–Hg–P angles (151.3(1), 148.5(2), 113.0(5)°) vary as expected from the above order.

Within the restrictions of varying solvents and temperatures the chemical shifts and coupling constants (Table 5) which have been shown to be sensitive to these effects [12, 19, 20] support the trend in donor characteristics and molecular parameters discussed previously. Thus $((2\text{-thienyl})_3P)_2HgCl_2$ which has the smallest P–Hg–P angle and longest

TABLE 4. Selected Molecular Parameters for $(R_3P)_2HgX_2$ (X = Cl, Br, I) Complexes

| | Hg–P (Å) | | PHgP (°) | Hg–X (Å) | | XHgX (°) | p$K_a$ for $R_3P$ [13] |
|---|---|---|---|---|---|---|---|
| $(Et_3P)_2HgCl_2$ [12] | 2.39(1) | 2.39(1) | 158.5(5) | 2.68(1) | 2.68(1) | 105.5(5) | 8.69 |
| $((NCC_2H_4)_3P)_2HgCl_2$ (I) [9] | 2.450(12) | 2.452(11) | 146.6(3) | 2.608(10) | 2.622(10) | 95.0(3) | 1.36 |
| (II) | 2.411(7) | 2.450(6) | 153.9(6) | 2.669(11) | 2.603(10) | 98.1(3) | |
| $((NCC_2H_4)_3P)_2HgBr_2\cdot Me_2CO$ [9] | 2.441(3) | 2.440(3) | 151.3(1) | 2.750(2) | 2.703(2) | 107.3(1) | 1.36 |
| $(EtMe_2P)_2HgBr_2$ [17] | 2.44(6) | 2.50(5) | 147(2) | 2.72(2) | 2.79(2) | 101.7(8) | 8.61 |
| | 2.39(5) | 2.48(6) | 150(2) | 2.79(3) | 2.88(2) | 106.9(8) | |
| $(Bu_3P)_2HgCl_2$ [17] | 2.3(6) | 2.6(6) | 139(2) | 2.55(5) | 2.66(5) | 105(2) | 8.43 |
| $(Ph_3P)_2HgCl_2$ [10] | 2.478(2) | 2.462(2) | 134.1(1) | 2.559(2) | 2.545(3) | 110.7(1) | 2.73 |
| $(Ph_3P)_2HgBr_2$ [10] | 2.535(15) | 2.540(16) | 113.0(5) | 2.633(6) | 2.626(8) | 106.9(3) | 2.73 |
| $(Ph_3P)_2HgI_2$ [18] | 2.557(3) | 2.574(3) | 108.95(9) | 2.733(1) | 2.763(1) | 110.43(4) | 2.73 |
| $((2\text{-}C_4H_3S)_3P)_2HgCl_2$ [11] | 2.472(2) | 2.513(2) | 128.6(1) | 2.539(2) | 2.519(2) | 107.3(1) | |

TABLE 5. $^{31}P$ NMR Data for Some $(R_3P)_2HgX_2$ Complexes

| Complex | δ (ppm) | $J$ ($^{199}Hg-^{31}P$) | Solvent | Temperature (°C) | Reference |
|---|---|---|---|---|---|
| $(Et_3P)_2HgCl_2$ | 38.0 | 5095 | $CDCl_3$ | 27 | 12 |
| $(Et_3P)_2HgBr_2$ | 32.2 | 4792 | $CDCl_3$ | 27 | 12 |
| $(Et_3P)_2HgI_2$ | 16.9 | 4033 | $CDCl_3$ | 27 | 12 |
| $((NCC_2H_4)_3P)_2HgCl_2$ | 44.4 | 5314 | $(CD_3)_2CO$ | 26 | this work |
| $((NCC_2H_4)_3P)_2HgBr_2$ | 17.6 | 5059 | $(CD_3)_2CO$ | 26 | |
| $((NCC_2H_4)_3P)_2HgI_2$ | 2.6 | 4154 | $(CD_3)_2CO$ | 26 | |
| $(EtMe_2P)_2HgCl_2$ | 16.0 | 5606 | $CDCl_3$ | −30 | 12 |
| $(EtMe_2P)_2HgBr_2$ | 13.1 | 5560 | $CDCl_3$ | −30 | 12 |
| $(EtMe_2P)_2HgI_2$ | 2.5 | 4778 | $CDCl_3$ | −40 | 12 |
| $(Bu_3P)_2HgCl_2$ | 28.9 | 5125 | $CDCl_3$ | 27 | 12 |
| $(Bu_3P)_2HgBr_2$ | 23.9 | 4829 | $CDCl_3$ | 27 | 12 |
| $(Bu_3P)_2HgI_2$ | 9.3 | 4089 | $CDCl_3$ | 27 | 12 |
| $(Ph_3P)_2HgCl_2$ | 28.1 | 4740 | $CH_2Cl_2$ | −43 | 19 |
| $(Ph_3P)_2HgBr_2$ | 21.7 | 4178 | $CH_2Cl_2$ | −43 | 19 |
| $(Ph_3P)_2HgI_2$ | 7.3 | 3073 | $CH_2Cl_2$ | −43 | 19 |
| $((2\text{-}C_4H_3S)_3P)_2HgI_2$ | −26.0 | 2722 | $CH_2Cl_2$ | −90 | 11 |
| $((2\text{-}C_4H_3O)_3P)_2HgCl_2$ | −37.5 | 4322 | $CH_2Cl_2$ | −90 | 11 |
| $((2\text{-}C_4H_3O)_3P)_2HgBr_2$ | −44.2 | 3540 | $CH_2Cl_2$ | −90 | 11 |

Hg–P bond of the chloro complexes has the smallest chemical shift and $^{199}Hg-^{31}P$ coupling constant whereas the $Et_3P$ and $(NCC_2H_4)_3P$ complexes have much larger chemical shifts, coupling constants, P–Hg–P angles and shorter Hg–P bonds. This trend further confirms that despite its low p$K_a$ value, 2-cyanoethylphosphine is a strong σ-donor as is $Et_3P$ to mercury(II) halides. The coupling constants and chemical shifts thus broadly follow the trend of increasing P–Hg–P angle and basicity of the phosphine as well as showing a general increase with increasing electronegativity of the halogen.

## Supplementary Material

Thermal parameters, observed and calculated structure factors have been deposited and are available from the authors on request.

## References

1 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 43* (1980) 87.

2 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 48* (1981) 185.

3 N. A. Bell, M. Goldstein, T. Jones, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 61* (1982) 83.

4 N. A. Bell, T. D. Dee, M. Goldstein and I. W. Nowell, *Inorg. Chim. Acta, 70* (1983) 215.

5 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 69* (1983) 155.

6 N. A. Bell, M. Goldstein, T. Jones and I. W. Nowell, *Inorg. Chim. Acta, 75* (1983) 21.

7 N. A. Bell, N. A. Chudley, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 141* (1988) 155.

8 N. A. Bell, L. A. March and L. W. Nowell, *Inorg. Chim. Acta, 156* (1989) 201.

9 N. A. Bell, M. Goldstein, L. A. March and I. W. Nowell, *J. Chem. Soc., Dalton Trans.,* (1984) 1621.

10 N. A. Bell, T. D. Dee, M. Goldstein, P. J. McKenna and I. W. Nowell, *Inorg. Chim. Acta, 71* (1983) 135.

11 D. W. Allen, N. A. Bell, S. T. Fong, L. A. March and I. W. Nowell, *Inorg. Chim. Acta, 99* (1985) 157.

12 N. A. Bell, T. D. Dee, P. L. Goggin, M. Goldstein, R. J. Goodfellow, T. Jones, K. Kessler, D. M. McEwan and I. W. Nowell, *J. Chem. Res. (S), 2(M)* (1981) 201.

13 C. A. Streuli, *Anal. Chem., 32* (1960) 985.

14 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch Press, Birmingham, 1974.

15 G. M. Sheldrick, *SHELX,* program for crystal structure determination, University of Cambridge, U.K., 1976.

16 A. Bondi, *J. Phys. Chem., 68* (1964) 441; D. Grdenic, *Q. Rev. Chem. Soc., 19* (1965) 303.

17 T. Jones, *Ph.D. Thesis,* Sheffield City Polytechnic, U.K., 1979.

18 L. Fälth, *Chem. Scr., 9* (1976) 71.

19 E. C. Alyea, S. A. Dias, R. G. Goel, W. O. Ogini, P. Pilon and D. W. Meek, *Inorg. Chem., 17* (1978) 1697.

20 S. O. Grim, P. J. Lui and R. L. Keiter, *Inorg. Chem., 13* (1974) 342.